

Modification thresholds in femtosecond laser processing of pure silica: review of dependencies on laser parameters [Invited]

B. Poumellec,^{1,*} M. Lancry,¹ A. Chahid-Erraji,¹ and P. G. Kazansky²

¹*Institut de Chimie Moléculaire et des Matériaux d'Orsay, UMR CNRS-UPS 8182, Université de Paris Sud 11, Bâtiment 410, 91405 Orsay, France*

²*Optoelectronics Research Centre, University of Southampton, Southampton, SO17 1BJ, UK*

**bertrand.poumellec@u-psud.fr*

Abstract: This review allows better defining the domains of macroscopic effects produced by the femtosecond laser irradiation in pure silica according to the laser parameters.

©2011 Optical Society of America

OCIS codes: (160.6030) Silica; (320.7130) Ultrafast processes in condensed matter; (350.3450) Laser-induced chemistry; (320.2250) Femtosecond phenomena.

References and links

1. B. Poumellec, M. Lancry, J. C. Poulin, and S. Ani-Joseph, "Non reciprocal writing and chirality in femtosecond laser irradiated silica," *Opt. Express* **16**(22), 18354–18361 (2008).
2. B. Poumellec, L. Sudrie, M. Franco, B. Prade, and A. Mysyrowicz, "Femtosecond laser irradiation stress induced in pure silica," *Opt. Express* **11**(9), 1070–1079 (2003).
3. R. S. Taylor, E. Simova, and C. Hnatovsky, "Creation of chiral structures inside fused silica glass," *Opt. Lett.* **33**(12), 1312–1314 (2008).
4. Y. Bellouard and M. O. Hongler, "Femtosecond-laser generation of self-organized bubble patterns in fused silica," *Opt. Express* **19**(7), 6807–6821 (2011).
5. P. Kazansky, W. Yang, E. Bricchi, J. Bovatsek, A. Arai, Y. Shimotsu, K. Miura, and K. Hirao, "Quill" writing with ultrashort light pulses in transparent materials," *Appl. Phys. Lett.* **90**(15), 151120 (2007).
6. D. N. Vitek, E. Block, Y. Bellouard, D. E. Adams, S. Backus, D. Kleinfeld, C. G. Durfee, and J. A. Squier, "Spatio-temporally focused femtosecond laser pulses for nonreciprocal writing in optically transparent materials," *Opt. Express* **18**(24), 24673–24678 (2010).
7. Y. Shimotsu, P. G. Kazansky, J. Qiu, and K. Hirao, "Self-organized nanogratings in glass irradiated by ultrashort light pulses," *Phys. Rev. Lett.* **91**(24), 247405 (2003).
8. M. Lancry, F. Brisset, and B. Poumellec, "In the heart of nanogratings made up during femtosecond laser irradiation," in *Bragg Gratings, Photosensitivity, and Poling in Glass Waveguides, OSA Technical Digest (CD)*, (Optical Society of America, 2010), ISBN 978-971-55752-55896-55754.
9. M. Ams, G. Marshall, P. Dekker, M. Dubov, V. Mezentssev, I. Bennion, and M. Withford, "Investigation of ultrafast laser-photon material interactions: challenges for directly written glass photonics," *IEEE J. Sel. Top. Quantum Electron.* **14**(5), 1370–1381 (2008).
10. K. Itoh, W. Watanabe, S. Nolte, and C. Schaffer, "Ultrafast processes for bulk modification of transparent materials," *MRS Bull.* **31**(08), 620–625 (2006).
11. J. Qiu, K. Miura, and K. Hirao, "Femtosecond laser-induced microfeatures in glasses and their applications," *J. Non-Cryst. Solids* **354**(12-13), 1100–1111 (2008).
12. M. Lancry, N. Grothoff, B. Poumellec, S. Guizard, N. Fedorov, and J. Canning, "Time-resolved plasma measurements in Ge-doped silica exposed to IR femtosecond laser," *Phys. Rev. B*. In Press.
13. F. Quéré, S. Guizard, and P. Martin, "Time-resolved study of laser-induced breakdown in dielectrics," *Europhys. Lett.* **56**(1), 138–144 (2001).
14. C. B. Schaffer, A. Brodeur, and E. Mazur, "Laser-induced breakdown and damage in bulk transparent materials induced by tightly focused femtosecond laser pulses," *Meas. Sci. Technol.* **12**(11), 1784–1794 (2001).
15. F. Quéré, S. Guizard, P. Martin, G. Petite, H. Merdji, B. Carré, J. Hergott, and L. Le Déroff, "Hot-electron relaxation in quartz using high-order harmonics," *Phys. Rev. B* **61**(15), 9883–9886 (2000).
16. B. Rethfeld, "Free-electron generation in laser-irradiated dielectrics," *Phys. Rev. B* **73**(3), 035101–035106 (2006).
17. S. Skupin and L. Bergé, "Self-guiding of femtosecond light pulses in condensed media: Plasma generation versus chromatic dispersion," *Physica D* **220**(1), 14–30 (2006).
18. A. Salimnia, N. T. Nguyen, S. L. Chin, and R. Vallée, "The influence of self-focusing and filamentation on refractive index modifications in fused silica using intense femtosecond pulses," *Opt. Commun.* **241**(4-6), 529–538 (2004).
19. A. Couairon, L. Sudrie, M. Franco, B. Prade, and A. Mysyrowicz, "Filamentation and damage in fused silica induced by tightly focused femtosecond laser pulses," *Phys. Rev. B* **71**(12), 125435 (2005).

20. L. Sudrie, "Propagation non-linéaire des impulsions laser femtosecondes dans la silice," Université de Paris Sud XI Orsay http://wwwy.ensta.fr/film/Archives/Theses_pdf/L_Sudrie (2002).
21. T. Kato, Y. Suetsugu, and M. Nishimura, "Estimation of nonlinear refractive index in various silica-based glasses for optical fibers," *Opt. Lett.* **20**(22), 2279–2281 (1995).
22. S. Le Boiteux, P. Segonds, L. Canioni, L. Sarger, T. Cardinal, C. Duchesne, E. Fargin, and G. Le Flem, "Nonlinear optical properties for TiO₂ containing phosphate, borophosphate, and silicate glasses," *J. Appl. Phys.* **81**(3), 1481–1487 (1997).
23. M. Lancry, N. Grothoff, S. Guizard, W. Yang, B. Pommellec, P. Kazansky, and J. Canning, "Femtosecond laser direct processing in wet and dry silica glass," *J. Non-Cryst. Solids* **355**(18–21), 1057–1061 (2009).
24. S. S. Mao, F. Quéré, S. Guizard, X. Mao, R. E. Russo, G. Petite, and P. Martin, "Dynamics of femtosecond laser interactions with dielectrics," *Appl. Phys., A Mater. Sci. Process.* **79**(7), 1695–1709 (2004).
25. S. Guizard, P. Martin, G. Petite, P. D'Oliveira, and P. Meynadier, "Time-resolved study of laser-induced colour centres in SiO₂," *J. Phys. Condens. Matter* **8**(9), 1281–1290 (1996).
26. P. P. Rajeev, M. Gertsyvolf, P. B. Corkum, and D. M. Rayner, "Field dependent avalanche ionization rates in dielectrics," *Phys. Rev. Lett.* **102**(8), 083001 (2009).
27. R. Taylor, C. Hnatovsky, and E. Simova, "Applications of femtosecond laser induced self organized planar nanocracks inside fused silica glass," *Laser Photonics Rev.* **2**(1–2), 26–46 (2008).
28. M. Lancry, B. Pommellec, A. Chahid-Er-raji, M. Beresna, and P. Kazansky, "Dependence of the femtosecond laser refractive index change thresholds on the chemical composition of doped-silica glasses," *Opt. Mater. Express*. In Press.
29. M. Lancry, B. Pommellec, and F. Brisset, "Ultrafast silica glass decomposition induced by femtosecond laser irradiation," in *12th International Symposium on Laser Precision Microfabrication*, (2011), <http://www.jlps.gr.jp/lpm/lpm2011/>.
30. P. Rajeev, M. Gertsyvolf, C. Hnatovsky, E. Simova, R. Taylor, P. Corkum, D. Rayner, and V. Bhardwaj, "Transient nanoplasmonics inside dielectrics," *J. Phys. B* **40**(11), S273–S282 (2007).
31. P. G. Kazansky, E. Bricchi, Y. Shimotsuma, and K. Hirao, "Self-Assembled Nanostructures and Two-Plasmon Decay in Femtosecond Processing of Transparent Materials," in *Conference on Lasers and Electro-Optics/Quantum Electronics and Laser Science Conference and Photonic Applications Systems Technologies*, (Optical Society of America, 2007), paper CThJ3.
32. R. Wagner, J. Gottmann, A. Horn, and E. W. Kreutz, "Subwavelength ripple formation induced by tightly focused femtosecond laser radiation," *Appl. Surf. Sci.* **252**(24), 8576–8579 (2006).
33. M. Lancry, B. Pommellec, W. Yang, and B. Bourguignon, "Oriented creation of anisotropic defects by IR femtosecond laser scanning in silica," *Opt. Express*, to be re-submitted.
34. R. Fleischer, P. Price, and R. Walker, "Solid-state track detectors: applications to nuclear science and geophysics," *Annu. Rev. Nucl. Sci.* **15**(1), 1–28 (1965).
35. C. Schaffer, A. Brodeur, N. Nishimura, and E. Mazur, "Laser-induced microexplosions in transparent materials: microstructuring with nanojoules," in *Proceedings of SPIE*, 143–147 (1999).
36. S. Juodkazis, K. Nishimura, S. Tanaka, H. Misawa, E. G. Gamaly, B. Luther-Davies, L. Hallo, P. Nicolai, and V. Tikhonchuk, "Laser-induced microexplosion confined in the bulk of a sapphire crystal: evidence of multimegabar pressures," *Phys. Rev. Lett.* **96**(16), 166101 (2006).
37. L. Sudrie, M. Franco, B. Prade, and A. Mysyrowicz, "Writing of permanent birefringent microlayers in bulk fused silica with femtosecond laser pulses," *Opt. Commun.* **171**(4–6), 279–284 (1999).
38. E. Bricchi, B. G. Klappauf, and P. G. Kazansky, "Form birefringence and negative index change created by femtosecond direct writing in transparent materials," *Opt. Lett.* **29**(1), 119–121 (2004).
39. A. Paleari, E. Franchina, N. Chiodini, A. Lauria, E. Bricchi, and P. G. Kazansky, "SnO₂ nanoparticles in silica: nanosized tools for femtosecond-laser machining of refractive index patterns," *Appl. Phys. Lett.* **88**(13), 131912 (2006).
40. V. R. Bhardwaj, E. Simova, P. P. Rajeev, C. Hnatovsky, R. S. Taylor, D. M. Rayner, and P. B. Corkum, "Optically produced arrays of planar nanostructures inside fused silica," *Phys. Rev. Lett.* **96**(5), 057404 (2006).
41. C. Hnatovsky, R. Taylor, P. Rajeev, E. Simova, V. Bhardwaj, D. Rayner, and P. Corkum, "Pulse duration dependence of femtosecond-laser-fabricated nanogratings in fused silica," *Appl. Phys. Lett.* **87**(1), 014104 (2005).
42. C. Hnatovsky, R. S. Taylor, E. Simova, V. R. Bhardwaj, D. M. Rayner, and P. B. Corkum, "Polarization-selective etching in femtosecond laser-assisted microfluidic channel fabrication in fused silica," *Opt. Lett.* **30**(14), 1867–1869 (2005).
43. C. Hnatovsky, R. Taylor, E. Simova, P. Rajeev, D. Rayner, V. Bhardwaj, and P. Corkum, "Fabrication of microchannels in glass using focused femtosecond laser radiation and selective chemical etching," *Appl. Phys., A Mater. Sci. Process.* **84**(1–2), 47–61 (2006).
44. W. Yang, E. Bricchi, P. G. Kazansky, J. Bovatsek, and A. Y. Arai, "Self-assembled periodic sub-wavelength structures by femtosecond laser direct writing," *Opt. Express* **14**(21), 10117–10124 (2006).
45. P. Kazansky, H. Inouye, T. Mitsuyu, K. Miura, J. Qiu, K. Hirao, and F. Starrost, "Anomalous anisotropic light scattering in Ge-doped silica glass," *Phys. Rev. Lett.* **82**(10), 2199–2202 (1999).
46. L. Sudrie, A. Couaïron, M. Franco, B. Lamouroux, B. Prade, S. Tzortzakakis, and A. Mysyrowicz, "Femtosecond laser-induced damage and filamentary propagation in fused silica," *Phys. Rev. Lett.* **89**(18), 186601 (2002).
47. W. Watanabe, T. Toma, K. Yamada, J. Nishii, K. Hayashi, and K. Itoh, "Optical seizing and merging of voids in silica glass with infrared femtosecond laser pulses," *Opt. Lett.* **25**(22), 1669–1671 (2000).
48. W. Yang, P. G. Kazansky, Y. Shimotsuma, M. Sakakura, K. Miura, and K. Hirao, "Ultrashort-pulse laser calligraphy," *Appl. Phys. Lett.* **93**(17), 171109 (2008).

49. M. Ams, G. D. Marshall, and M. J. Withford, "Study of the influence of femtosecond laser polarisation on direct writing of waveguides," *Opt. Express* **14**(26), 13158–13163 (2006).
50. D. J. Little, M. Ams, P. Dekker, G. D. Marshall, J. M. Dawes, and M. J. Withford, "Femtosecond laser modification of fused silica: the effect of writing polarization on Si-O ring structure," *Opt. Express* **16**(24), 20029–20037 (2008).
51. H. R. Reiss, "Polarization effects in high-order multiphoton ionization," *Phys. Rev. Lett.* **29**(17), 1129–1131 (1972).
52. V. V. Temnov, K. Sokolowski-Tinten, P. Zhou, A. El-Khamhawy, and D. von der Linde, "Multiphoton ionization in dielectrics: comparison of circular and linear polarization," *Phys. Rev. Lett.* **97**(23), 237403 (2006).
53. D. Liu, Y. Li, M. Liu, H. Yang, and Q. Gong, "The polarization-dependence of femtosecond laser damage threshold inside fused silica," *Appl. Phys. B* **91**(3-4), 597–599 (2008).
54. B. Poumellec and M. Lancry, "Damage thresholds in femtosecond laser processing of silica: a review," in *Bragg Gratings, Photosensitivity, and Poling in Glass Waveguides, OSA Technical Digest (CD)*, (Optical Society of America, 2010), ISBN 978-971-55752-55896-55754.
55. C. Schaffer, A. Brodeur, and E. Mazur, "Laser-induced breakdown and damage in bulk transparent materials induced by tightly focused femtosecond laser pulses," *Meas. Sci. Technol.* **12**(11), 1784–1794 (2001).
56. L. Shah, A. Arai, S. Eaton, and P. Herman, "Waveguide writing in fused silica with a femtosecond fiber laser at 522 nm and 1 MHz repetition rate," *Opt. Express* **13**(6), 1999–2006 (2005).
57. G. Cheng, K. Mishchik, C. Maclair, E. Audouard, and R. Stoian, "Ultrafast laser photoinscription of polarization sensitive devices in bulk silica glass," *Opt. Express* **17**(12), 9515–9525 (2009).
58. L. Sudrie, M. Franco, B. Prade, and A. Mysyrowicz, "Study of damage in fused silica induced by ultra-short IR laser pulses," *Opt. Commun.* **191**(3-6), 333–339 (2001).
59. J. W. Chan, T. Huser, S. Risbud, and D. M. Krol, "Structural changes in fused silica after exposure to focused femtosecond laser pulses," *Opt. Lett.* **26**(21), 1726–1728 (2001).
60. J. Chan, T. Huser, S. Risbud, and D. Krol, "Modification of the fused silica glass network associated with waveguide fabrication using femtosecond laser pulses," *Appl. Phys., A Mater. Sci. Process.* **76**(3), 367–372 (2003).
61. W. J. Reichman, J. W. Chan, C. W. Smelser, S. J. Mihailov, and D. M. Krol, "Spectroscopic characterization of different femtosecond laser modification regimes in fused silica," *J. Opt. Soc. Am. B* **24**(7), 1627–1632 (2007).
62. N. Nguyen, A. Saliminia, S. Chin, and R. Vallée, "Control of femtosecond laser written waveguides in silica glass," *Appl. Phys. B* **85**(1), 145–148 (2006).
63. V. R. Bhardwaj, P. B. Corkum, D. M. Rayner, C. Hnatovsky, E. Simova, and R. S. Taylor, "Stress in femtosecond-laser-written waveguides in fused silica," *Opt. Lett.* **29**(12), 1312–1314 (2004).
64. T. Tamaki, W. Watanabe, H. Nagai, M. Yoshida, J. Nishii, and K. Itoh, "Structural modification in fused silica by a femtosecond fiber laser at 1558 nm," *Opt. Express* **14**(15), 6971–6980 (2006).
65. D. Homoelle, S. Wielandy, A. L. Gaeta, N. F. Borrelli, and C. Smith, "Infrared photosensitivity in silica glasses exposed to femtosecond laser pulses," *Opt. Lett.* **24**(18), 1311–1313 (1999).
66. S. Onda, W. Watanabe, K. Yamada, K. Itoh, and J. Nishii, "Study of filamentary damage in synthesized silica induced by chirped femtosecond laser pulses," *J. Opt. Soc. Am. B* **22**(11), 2437–2443 (2005).
67. I. Burakov, N. Bulgakova, R. Stoian, A. Mermillod-Blondin, E. Audouard, A. Rosenfeld, A. Husakou, and I. Hertel, "Spatial distribution of refractive index variations induced in bulk fused silica by single ultrashort and short laser pulses," *J. Appl. Phys.* **101**(4), 043506 (2007).
68. J. B. Ashcom, R. R. Gattass, C. B. Schaffer, and E. Mazur, "Numerical aperture dependence of damage and supercontinuum generation from femtosecond laser pulses in bulk fused silica," *J. Opt. Soc. Am. B* **23**(11), 2317–2322 (2006).
69. N. T. Nguyen, A. Saliminia, W. Liu, S. L. Chin, and R. Vallée, "Optical breakdown versus filamentation in fused silica by use of femtosecond infrared laser pulses," *Opt. Lett.* **28**(17), 1591–1593 (2003).
70. S. Lee and S. Nikumb, "Characteristics of filament induced Dammann gratings fabricated using femtosecond laser," *Opt. Laser Technol.* **39**(7), 1328–1333 (2007).
71. K. Yamada, W. Watanabe, T. Toma, K. Itoh, and J. Nishii, "In situ observation of photoinduced refractive-index changes in filaments formed in glasses by femtosecond laser pulses," *Opt. Lett.* **26**(1), 19–21 (2001).
72. E. Bricchi, "Femtosecond laser micro-machining and consequent self-assembled nano-structures in transparent materials," PhD thesis 30234 (2005).
73. K. Itoh and W. Watanabe, "Toward nano-and microprocessing in glass with femtosecond laser pulses," *RIKEN Rev.* 90–94 (2003).
74. J. B. Ashcom, R. R. Gattass, C. B. Schaffer, and E. Mazur, "Numerical aperture dependence of damage and supercontinuum generation from femtosecond laser pulses in bulk fused silica," *J. Opt. Soc. Am. B* **23**(11), 2317–2322 (2006).
75. C. Hnatovsky, R. S. Taylor, E. Simova, P. P. Rajeev, D. M. Rayner, V. R. Bhardwaj, and P. B. Corkum, "Fabrication of microchannels in glass using focused femtosecond laser irradiation and selective chemical etching," *Appl. Phys., A Mater. Sci. Process.* **84**(1-2), 47–61 (2006).
76. P. Kazansky, "Recent advances in modification of optical materials by strong fields: from poling to femtosecond laserwriting," in *Conference on Lasers and Electro-Optics/Pacific Rim*, (Optical Society of America, 2009), paper ThA4_1.

1. Introduction

Silica-based glasses serve in the backbone of many of today's rapidly expanding photonics applications. Current advanced femtosecond laser systems offer a myriad of material interactions in glassy media; from surface machining, annealing, 3D refractive index changes profiling (positive or negative index change; isotropic or anisotropic) depending on both the laser parameters and the material chemical composition. Recently, other properties have also arisen, like chirality [1–3], directional dependence writing [1,2,4–6], nanogratings [7], glass decomposition [8]. To our knowledge, no other technique holds the potential to realize 3D multi-functional photonic devices, fabricated in one single step in a variety of transparent materials. These interactions exhibit enormous potentialities in the development of a new generation of components for micro-optics, telecommunications, 3D optical data storage, imaging, biophotonics and so many more [9–11]. However, while ultra-fast lasers offer exciting prospects for 3D shaping of photonic components, there are some drawbacks in using them for large scale micromachining. In addition even if many results have been already reported in SiO₂, the processing windows are, as yet, poorly defined. Authors investigated refractive index changes, etching rates, permanent absorptions, stresses, nanostructure appearance according to the laser pulse energy, pulse duration, numerical aperture and writing velocity etc. From these results, it is possible to identify various regimes with at least 3 modification thresholds in SiO₂ glass. Looking inside the laser track, in the direction of writing laser propagation, there is the appearance of permanent isotropic positive index change, the appearance of a strong (up to a few 10⁻²) linear birefringence and lastly the formation of voids.

The obvious laser parameters are: the laser light wavelength, the light intensity at the point of laser interaction with the matter, the duration of the pulse, the repetition rate of the pulses, the duration of the irradiation (or the scanning speed vs the repetition rate for a non-static exposure). However, these parameters are not all relevant of the processes we want to discuss and moreover there are additional parameters. For identifying them, we have to recall some information already known about the interaction mechanisms of the ultrafast laser with pure silica.

2. The Electron Excitation and the Interaction Volume

As the laser pulse energy is high enough, multiphoton absorption is the primary cause of energy transfer to the glass. In this case, it is possible to achieve interband transitions in transparent materials without the need of doping that leads to linear absorption at the pump wavelength. Specifically in pure silica glass, for the IR laser Ti:Al₂O₃ emitting at 800nm, it needs 6 photons [12,13] for an electron to transit from valence band to conduction one. In such a case, multiphoton ionization (MPI) leads to electron-hole pairs formation. This is well described in [14]. Once the free electron density in the conduction band has become non-zero, further absorption increases the kinetics energy of the electron plasma i.e. its temperature (typ. up to 30eV in SiO₂ [15] but most of them have less than 10 eV in our conditions). Electron collision between accelerated electrons and valence ones can also increase the plasma density. In the range of intensity discussed in this paper, the electron excitation by tunneling seems to be not working [16].

Usually, the experiments are performed by focusing the laser beam a few hundreds microns into the glass by means of a lens. Then, the beam is moved transversally (usually) or longitudinally (more scarcely). Because the shape of the interaction volume changes on laser parameters, the light intensity distribution in this volume changes influencing the energy threshold [17]. It is a combination of optical and physical processes. It changes with the focusing strength and the interaction region exhibit different shapes.

It is therefore, necessary to define the interaction not only by the energy intensity but by also the numerical aperture (NA) of the lens used to focus the beam into the material.

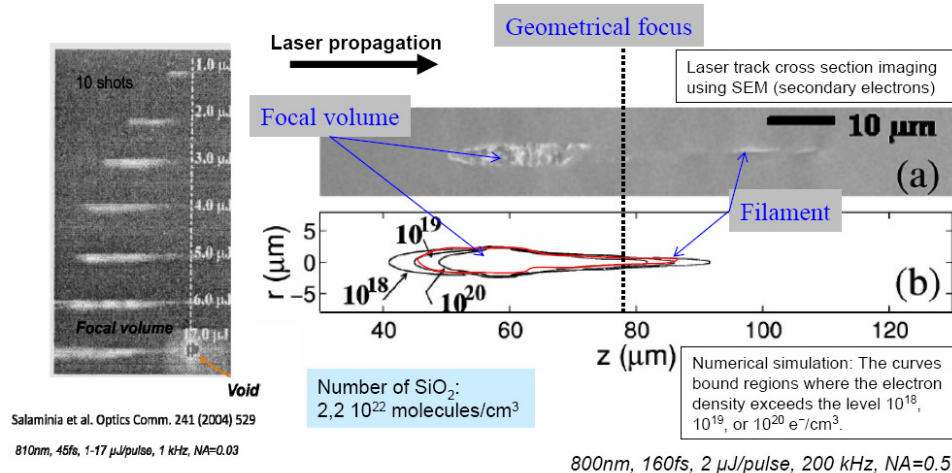
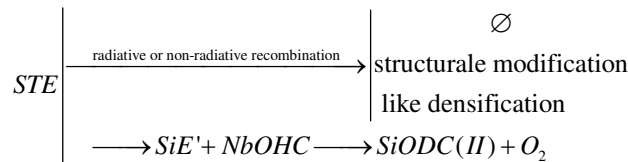


Fig. 1. Shape of the interaction volume. (On the left side, Fig. 1(a)) Shape of the interaction volume according to pulse energy in the case of weak focusing. It is detected thanks to supercontinuum emission. The dashed white line is the geometrical focus. The laser is coming from the left hand side. From Salaminia et al. [18]. Laser parameters: 1-17 μJ, NA = 0.03, 45 fs, 1 kHz, 810 nm. (On the right side, Fig. 1(b)) Shape of the interaction volume for pulse energy 2 μJ in the case of strong focusing and with filamentation. This simulation is from Ref [19,20]. The laser is coming from the left side. Laser parameters: 1-17 μJ, NA = 0.5, 160 fs, 200 kHz, 800 nm.

Furthermore, the NA does not alone define the focusing but the power intensity in the beam itself plays also a role in the focusing (index is non-linear: $n = n_0 + n_2 I_{loc}$, $n_2 = 3.2 \cdot 10^{-16} \text{ cm}^2/\text{W}$) [21,22]. Increasing the beam energy results therefore in the displacement of the focus to the sample entrance face (Fig. 1(a)) and the interaction volume become elongated before the geometrical focus (linear focus). Above a critical beam energy ($P_{CR} = \frac{\lambda^2}{2\pi n_0 n_2}$), a non diverging trace beyond the geometrical focus appears (see Fig. 1(b)). This is due to a balance between the non-linear increase of the refractive index and the defocusing effect of the electron plasma [14]. In conclusion, the power intensity is no longer an input parameter of the experiment but the beam power or the beam energy is. We have therefore to classify the experiments according to: laser pulse energy, NA, pulse duration instead of light intensity even if in a point, intensity is the relevant parameters for material change.

3. The Relaxation Processes and the Effect in the Material: the Threshold Definitions

Glass modifications are the result of relaxation of photo-excited electron. Electrons relax first into self-trapped excitons (STE) by electron-phonon coupling and then annihilate radiatively (lifetime of nanoseconds at room temperature) or not (coupling with lattice phonons), or transform into point defects (e.g. into SiE' and NBOHC (bond breaking) and then into a silicon oxygen deficient center quoted as SiODC(II)) [23,24] following the reaction scheme sketched below:



The yield for defect production is small [25] compared to the other ways but nevertheless can play a striking role in memory effect [26,27]. The first observation we can report under

irradiation powerful enough is the transmission decrease. It is observed on a large wavelength range from IR to blue [19,20]. This reveals that glass is modified in its extended microstructure. We speculate that such glass modification is the results of electron energy transmitted to the lattice by non-radiative coupling of electron with the lattice. This coupling corresponds to an increase of non-equilibrium temperature of the lattice that can reach several thousands of degrees in the illuminated area limited by thermal conduction [28]. The increase of temperature should be long enough (i.e. longer than the glass relaxation time [28]) for transforming the glass and this defines a first threshold.

Considering that the energy density (W) finally transferred to the lattice is expressed as the product of (a), of the forbidden energy gap E_g of the glass and of the STE concentration at the end of the pulse i.e. $W = a \cdot E_g \cdot [STE]$ where a is an enhancing coefficient taking into account the acceleration energy after interband excitation of the electrons. Considering also that only a fraction α of the incident energy is absorbed by the matter due to partial reflection by the plasma [24], e.g. for 0.55NA, 160fs, 100kHz, 800nm, the proportion is fixed to 23%. In these conditions, for 0.1 μ J (value of the threshold for these parameters), the rough estimate of the fictive temperature is 2490°C [28]. Because STE production is the result of MPI in our case, the STE concentration varies as $N_o \cdot \sigma \cdot I_{T1}^6 \cdot \tau \cdot \sigma = 4.5 \cdot 10^{-69} \text{ s}^{-1} \text{ cm}^{12} \text{ W}^{-6}$ [12], I_{T1} the intensity threshold corresponding to T1 threshold in silica, N_o the density of states at the top of valence band. In sum-up, the minimum energy density required for glass modification defined W , from that we get the intensity threshold I_{T1} . I_{T1}/α is the light intensity that should arrive at the absorption point. Then from non-linear propagation law, we deduce the T1 energy of the beam thanks to a relation described by Schaffer et al. [12].

T2 threshold exhibits a totally different origin than T1. It is the onset of a strong linear birefringence (typ. 10^{-2}) based on the appearance of a long range microstructure i.e. the assembly of nanoplanes that sometimes organize in quasi-periodic nanogratings [7]. Nanoplanes (a few 10's nm thick) are composed by porous matter [8] that on the average has a lower atomic density than the surrounding glass. They are formed as a result of glass decomposition with oxygen releasing into nanopores [29]. The appearance of nanoplanes, the orientation of which being determined by laser polarization, seems related whatever the interpretation (nanoplasma [30], photon-plasmons interference [31] or self-organization alike Turing structure), to large fluctuation of plasma density or energy. It has been noted that it needs several pulses for their observation, the number depending on the pulse energy. On the other hand, we have observed them at a repetition rate as low as 1 kHz [29] so with pulses without other relation than some information "written" in the glass. On the other hand, periodic nanostructures can be prolonged regularly on a long distance (several mm) [32]. It is therefore clear that the plasma micro-structure is recorded in the glass and that the corresponding information seeds the plasma structure in the subsequent pulse. Referring to the relaxation scheme already sketched for T1 interpretation, we will hypothesize that point defects, even if they are not the most efficient relaxation pathway are good candidates for recording medium. As a matter of fact, decomposition of silica leads to SiODC(II) defect formation [33], which may behave as trapping centers and then to electron source for the next pulse. Therefore, in the process of multiphoton ionization, these centers with occupied level in the forbidden gap are expected to be readily ionized in first, contributing to plasma nanostructure formation. As the irradiation is going on, the process self-organized into a stable structure.

In such a case, the spatial overlap between two consecutive pulses is a necessary condition for regular "writing" of the periodic nanostructures. More quantitatively, we may consider that birefringence is always detected above the same quantity (quoted as $[B]$). This minimal quantity is certainly proportional to an amount of glass decomposition which is itself proportional to the branching ratio (ϵ) from STE on the one hand and to STE concentration on the other hand ($[STE]$) produced by a series of pulses (n_p). We may write $[B] \sim n_p \cdot \epsilon \cdot [STE]$. On

the other hand, $[STE] \sim N_o \sigma \cdot I^k \tau$ where k is the number of photons in the MPI process. So, finally I_{T2} corresponding to $T2$ varies as $(n_p \varepsilon N_o \sigma \tau)^{-1/6}$ [28].

For large pulse energies, voids in glass are achievable by photo irradiation. It is relevant of a mechanism that it is called Coulombian explosion. The model has been suggested firstly by Fleischer et al. in 1965 [34] and is also reported more recently by [35,36]. The mechanism at the basis of void formation is briefly the following. When the density of excitations at a point in the matter is very large (the electrons have been pushed away due to e.g. ponderomotive force), the Coulombian force between ions can overcome their binding energy. In that case, ions are also pushed away for occupying interstitial positions in the surrounding mater. It results the formation of a cavity surrounded by a shell of high density. The corresponding energy threshold is called $T3$ in the paper.

3.1 Experimental Measurement of $T1$

The first modification threshold is usually associated to optical breaking (OB) but it is better defined by the permanent decrease of the transmission at the pump wavelength. An example can be found in [19,20]. When one follow the transmission along the time, it decreases strongly under the pulse irradiation, this is due to the plasma formation but this absorption disappears with the plasma. Then, after the pulse, there can remain an absorption showing the formation of permanent damages. If we plot the level of absorption after the pulse, we can see that the threshold for this first criterion is $0.1 \mu J$ for $NA = 0.5$, 160 fs, 100 kHz, 800 nm [19,20]. This decrease of transmission is accompanied by an increase of refractive index in the laser trace. This last is mainly isotropic (there is still a small stress induced birefringence that accompanies the permanent densification) and easily detected by observations through the sample by means of an optical microscope following the direction of writing laser propagation. Other properties like the etching rate increase can be used for OB threshold determination.

3.2 Experimental Measurement of $T2$

If we increase the energy enough, a strong linear birefringence appears in pure silica [37]. This birefringence is spectacular. Its orientation is imprinted by the polarization of the writing laser [38]. It exists either for low or high NA but seems specific of silica. For instance, in SiO_2-SnO_2 , (16 mol %) no birefringence is detected and in addition the index change is positive contrarily to pure silica [39]. The phenomenon is certainly related to the formation of nanostructures (series of nanoplasms of low density in the laser tracks. These ones have been discovered by Kazansky group in first [7] and confirmed by several authors, specifically by Hnatovsky group [40–43]. They arise from modulation of chemical composition [7], through oxygen segregation [29]. The nanoplasms are usually not periodically organized but sometimes the regularity is spectacular [44]. Depending on the authors, it could be related to stationary density waves in the plasma produced by interference between plasmon and light waves or by self-organization [27]. This phenomenon explained other experimental facts than only form birefringence, e.g. Anomalous light scattering along light polarization [45], linear dichroism [46] etc.

3.3 Experimental Measurement of $T3$

When pulse energy is increased further (e.g. $>1-2 \mu J$, $>0.3NA$, $>130fs$, 800 nm), it is possible to produce holes in silica and then by a subsequent slight decrease of the pulse energy [47], to move these holes and even to merge a hole into another.

In conclusion of this section, the light intensity is finally not a good parameter for the experiments and we have to replace it by pulse energy in the beam and by the numerical aperture of the concentrating lens. On the other hand, the duration of the irradiation has to be replaced by the writing speed. Additional parameters are: what we call the configuration (i.e. the laser polarization direction versus the beam scanning one, quoted $(\vec{e}, \vec{v})$), the scanning mode (transversal if the scanning is perpendicular to the light propagation or longitudinal

when the scanning is parallel, the first mode is used extensively). The depth of focusing could be also a relevant parameter since the shape of the interaction length changes on it, but we have not found studies of thresholds dependencies on that parameter. It is the same issue concerning the scanning direction versus the laser compressor plane. Only a few papers deal with this problem [1,6,48]. These two last parameters are thus excluded of our set which is finally: *the pulse energy, the numerical aperture, the duration of the pulse, the repetition rate of the pulses, the laser wavelength, the scanning speed and the writing configuration*. They are recalled each time it is necessary in the paper.

4. Dependencies

4.1 Dependence on the Type of Light Polarization (Linear or Circular) and the Writing Configuration ($\vec{e}, \vec{v}$)

About T1, it has been observed that ultrafast-laser written waveguides exhibit a different refractive index change depending on whether the polarization of the ultrafast laser pulses was linear or circular under otherwise identical writing conditions [49,50]. This behavior implies that the energy absorbed is polarization-dependent. Little et al (this special edition), hypothesize that the polarization dependence of photo-ionization cross-sections is at the origin of this behavior.

It has been established theoretically and experimentally that the relative photo-ionization cross-sections for linearly and circularly polarized beams (denoted σ_l and σ_c respectively) is most strongly dependent on the multiphoton order, n , which is defined as the number of photons for exciting an electron across the energy band gap of the glass [51,52]. Reiss identified three behavioral regimes and for silica for which 6 photons are required, we expect $\sigma_c/\sigma_l < 1$. In the context of ultrafast-laser modification, these behavioral regimes can be identified by comparing the refractive index change induced by linearly (LP) and circularly polarized (CP) pulses. A second factor influencing whether circularly or linearly polarized pulses yield a higher index change is the power density ([52], 10 TW/cm², 50fs, 800nm: linear stronger). However, we have found only one paper relative to threshold dependence on polarization state [53]. They found index changes from CP or LP light equal for NA<0.22. For NA = 0.22 and pulse duration smaller than 230fs, LP>CP. As most of the results are with linear polarization, our review has been restricted accordingly.

About configuration effect influence ($\vec{e}, \vec{v}$), for writing speed between 10 and 1500 $\mu\text{m/s}$ and repetition rate between 1kHz and 500 kHz, we have not found significant difference between the two configurations (polarization parallel or perpendicular to the beam scanning orientation (transversal writing)) as we can see in the Fig. 2.

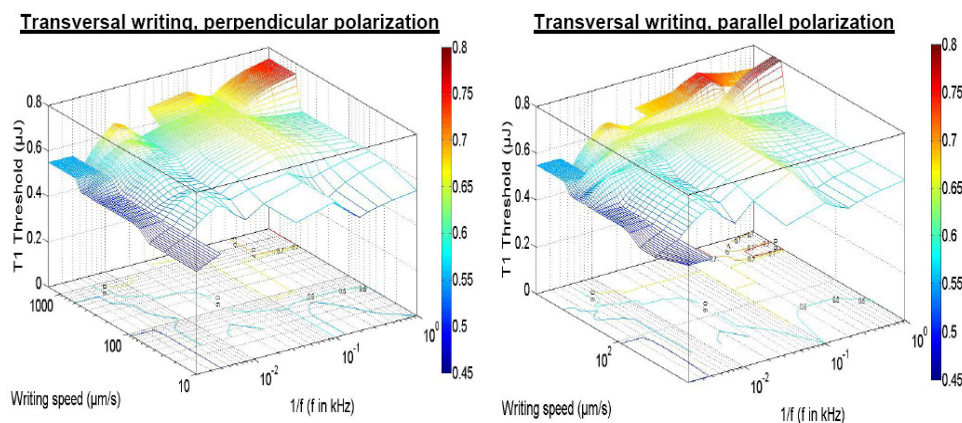


Fig. 2. T1 measurement in the conditions 0.5NA, 280fs, 1030nm, 10-1000 $\mu\text{m/s}$, 1-500kHz, 250 μm deep.

We are thus in agreement with Hnatovsky [41] (0.65NA, 40fs, 100kHz, 800nm, 30μm/s). We will see in section 4.4 that for pulse duration larger than 200 fs, for 0.5NA, T2 coincides with T1. We have thus observed that T2 is also not dependent on configuration. We are in agreement, here for T2, with Hnatovsky [41] (0.65NA, 40fs, 100kHz, 800nm, 30μm/s) and with Bhardwaj [40] (0.65NA, 50fs, 100kHz, 800nm, 30μm/s) but our pulse duration is different. On the contrary, coupling birefringence measurements and SEM observations for 0.55NA, 160fs, 100kHz, 800nm, 100μm/s, we found $T1 = 0.17 \pm 0.05 \mu J$ for $\vec{e} \perp \vec{v}$ and 0.31 ± 0.03 for $\vec{e} // \vec{v}$ [54]. Therefore, this is not clear matter at the moment and as most of the studies are for parallel configuration, we went on our analysis of the literature mainly with *parallel configuration* excepted special mention.

4.2 Dependence of T1 on the Laser Wavelength

A first result is from Schaffer et al. [55]. Parameters are 0.65NA, 110fs, 1kHz, 400 and 800 nm, static. The variation of threshold intensity is weak on laser wavelength, 2.9 and $3.2 \cdot 10^{13} \text{ W/cm}^2$. This corresponds to an increase of T1 from 3.7nJ to 16nJ from 400 and 800 nm. A second result is from Shah et al. [56]. Laser parameters are, 0.85NA, 1kHz, with 500 fs at 522nm and with 375fs at 1045nm, 50μm/s-10mm/s, $\vec{e} // \vec{v}$ (note that pulse duration leads to $T1 = T2$, see section 4.4). In that case, T1 is varying weakly, just between 0.07 and 0.10 μJ/pulse for wavelength changing from 522 to 1045 nm.

Another result is from us with 0.60NA, 110fs, 1kHz, 10μm/s, $\vec{e} // \vec{v}$. In these conditions, $T1 = T2$. We found at 400 nm, thresholds at 0.018-0.032 μJ, whereas at 800 nm, they are at 0.0465-0.050 μJ. These measurements parameters are very close to the one of Schaffer et al. and so in good agreement. In contrast, Shah et al. is a result quite different. The only difference [55] in the laser parameter set seems to be the scanning speed: static for Schaffer or 10μm/s for us and larger speed for Shah et al. [56]. So, maybe the wavelength sensitivity is revealed just below a scanning speed limit. This remains to be confirmed by more experiments.

Yang et al. [44] made the same measurement but in perpendicular configuration ($\vec{e} \perp \vec{v}$), and 0.32NA, 500fs, 200kHz, 200μm/s. They found $T2 = 0.15 \mu J$ at 532 nm, and $T2 = 0.4 \mu J$ at 1045 nm. Although laser parameter set is a bit different than previous one, especially the configuration is not the same, this experiment confirms that the threshold increases with larger wavelength. The origin of this dependence is partly accounted for by Schaffer et al. [55]. They gave a relation based on optical propagation properties only:

$$\frac{E_{th}}{\tau} = \frac{I_{th} \lambda^2}{\pi(NA)^2 + I_{th} 2\pi n_0 n_2}.$$

All results are only approximately in agreement with this relation revealing that I_{th} probably depends also on wavelength. Therefore, we processed our analysis of the literature in taking into consideration results measured at 800 nm, the most common laser wavelength used in the literature.

4.3 Dependence on Writing Speed and Repetition Rate

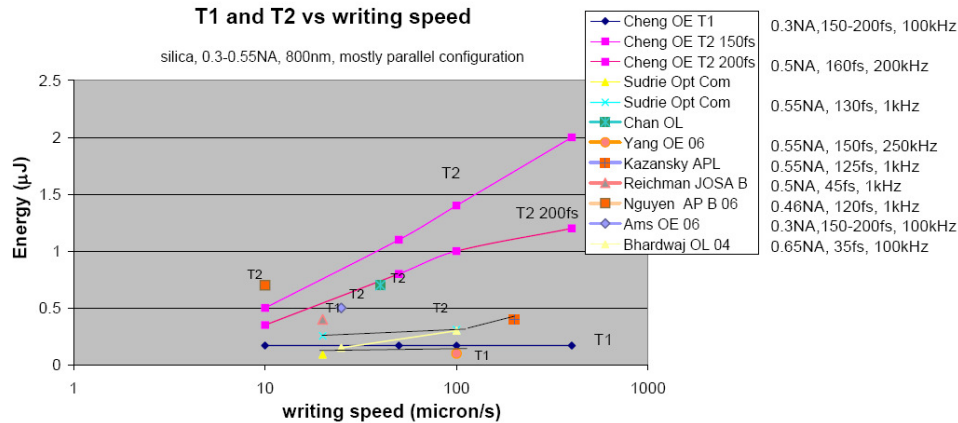


Fig. 3. Dependence of T1 and T2 on the writing speed choosing NA between 0.3 and 0.55. Ref are the following: Cheng OE [57], Sudrie Opt Com [37,58], Chan OL [59,60], Yang OE [44], Kazansky APL [5], Reichman JOSAB [61], Nguyen APB 06 [62], Ams OE 06 [49], Bhardwaj OL 04 [63].

It is difficult to find clear conclusion from the Fig. 3 that collects data for NA around 0.3 to 0.55 of the dependence of thresholds on writing speed. T1 seems to be weakly dependent on writing speed. Whatever the parameters, it remains below 0.2 for this NA excepted for Reichman et al. [61] (0.4μJ). On the other hand, we show in section 4.1 with 0.5NA, 280fs, 1030nm, 10-1000μm/s, 1-500kHz that T1 is weakly varying standing at the level of 0.5-0.6μJ. This is in agreement with Tamaki [64], (0.55NA, 950fs, 1558nm, 2 μm/s, parallel configuration) that found in addition a weak dependence on repetition rate. On the contrary, there are contradictory results for longitudinal writing. Cheng et al. [57] found no dependence whereas Homoelle et al. [65] found an increase of one order of magnitude passing from 0.4 to 4μJ for 5 to 400 μm/s (5-400 μm/s, 0.16NA, 60fs, 1kHz, 800 nm, longitudinal writing).

We can make similar remarks for T2 (Fig. 4). It seems that for high repetition rate (100-250 kHz), there is a weak dependence on writing speed and value below 0.5μJ. On the contrary dependence appears much larger for Cheng et al. [57] and for N'Guyen et al. [62]: a factor 4 from 10 to 1000μm/s. This discrepancy seems to arise from the writing mode that is longitudinal for them. For 1kHz, values appear also above 0.5μJ for several authors. There is almost none available information about dependency on repetition rate. For tentatively clearing this point, we have performed additional measurement in transversal writing with 0.5NA, 280fs, 1030nm, 10-1500μm/s, 1-500kHz (see Fig. 4).

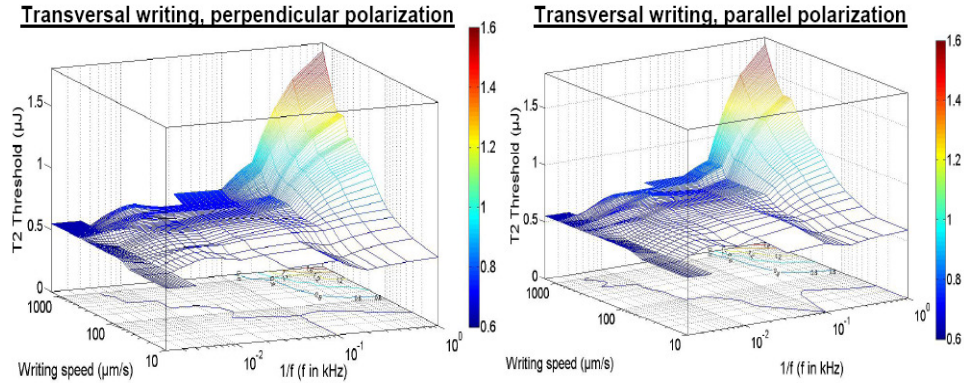


Fig. 4. T2 threshold in transversal writing with 0.5NA, 280fs, 1030nm, 10-1000μm/s, 1-500kHz

As we can see, there is no dependence on either writing speed or repetition rate over a large domain where $T1 = T2$. A separation between them appears for large speed and low frequency. On the other hand, Yang et al. [44] found that T2 might depend on the ratio v/f in varying speed of writing and repetition rate following the same scale in such a way their ratio remains constant with 0.29NA, 500fs, 1045nm, $\vec{e} \perp \vec{v}$: 0.4μJ for 100 μm/s and 100 kHz, 0.6μJ for 300 μm/s and 300 kHz, 0.4μJ for 500 μm/s and 500 kHz, 0.4μJ for 1000 μm/s and 1000 kHz. In addition, Wagner et al. experiments ([32] but at the surface) suggest that nanostructures might depend on overlapping between two consecutive pulses.

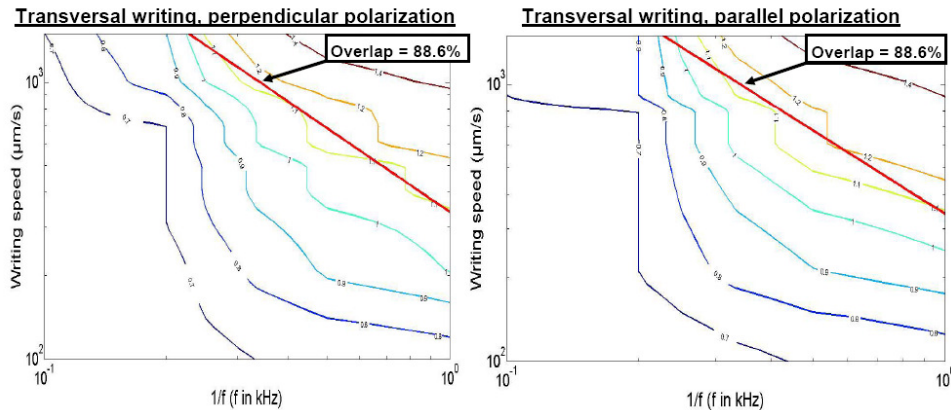


Fig. 5. contour plot extracted from Fig. 4 for low repetition rate and large speed. The red line is an iso-overlap (88.6%) according to $1-v/(\varnothing.f)$ where $\varnothing$ is the diameter of the interaction volume taken equal to 3μm.

The similarity of the contour curves (Fig. 5) with the overlap one seems to confirm that the overlap is a relevant parameter linking writing speed and repetition rate. By comparison with our measurements, we may deduce that T2 increases when overlap departs a few % from 1. This is an important conclusion for industrial use of the birefringence. Of course this conclusion applies only for transversal writing.

4.4 Dependence on Pulse Duration

Measurements of threshold dependency on pulse duration have been performed in first by [41], Fig. 6 shows the results. In these experiments, the fs pulse temporal broadening due to group-velocity dispersion in the microscope objective is compensated by pre-chirping the

laser pulse in the compressor. Thresholds appear to be mostly independent on pulse duration by plateau. For the parameters used in Fig. 6, T1 is equal to 40 nJ for pulse duration smaller than 170fs and 80nJ above. Moreover, T2 is separated from T1 for duration smaller than 170fs. We observe also that T3 is independent on pulse duration above but strongly dependent below 200fs.

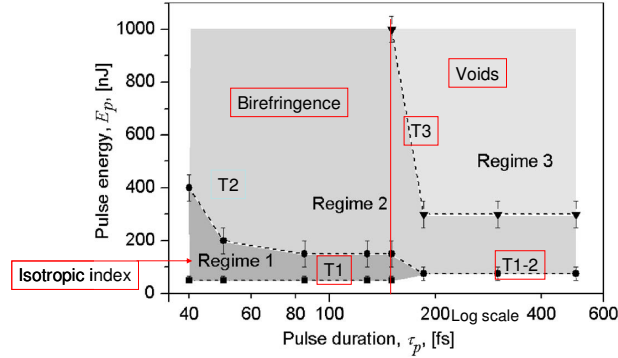


Fig. 6. Pulse energy versus pulse duration diagram in semi log scale defining regions with different kinds of laser interaction with silica after [41]. Laser parameters: 0.1-1 μ J, NA = 0.65, 40-500 fs, 100 kHz, 800 nm, 30 μ m/s, perpendicular configuration, 100 μ m focus depth. The red line indicates the intersection with the NA diagram (for 160 fs).

There are other results on pulse duration dependency that we can compare. They are collected in Fig. 7. The shift between them can be explained by the different NA used. In such a way, the difference on T1 between Onda [66] and Hnatovsky [41] is due to $NA^{-1.9}$ (see section 4.5). Whatever NA, authors agree on T1 different from T2 for lower pulse duration and T1 = T2 for large ones. The pulse duration value for separation decreases when NA increases: 170fs for NA = 0.65, around 220fs for NA = 0.22 and 250fs for NA = 0.1. Theoretically, from Schaffer et al. if we refer to optical propagation argument valid for strong focusing, T1 should increase linearly on pulse duration, as the beam power is a relevant parameter: $\frac{E_{th}}{\tau} = \frac{I_{th}\lambda^2}{\pi(NA)^2 + I_{th}2\pi n_0 n_2}$. Actually, it is not. So, we can suspect that light intensity changes accordingly, decreasing discontinuously on pulse duration for this NA i.e. $I_{th}\cdot\tau \approx cte$.

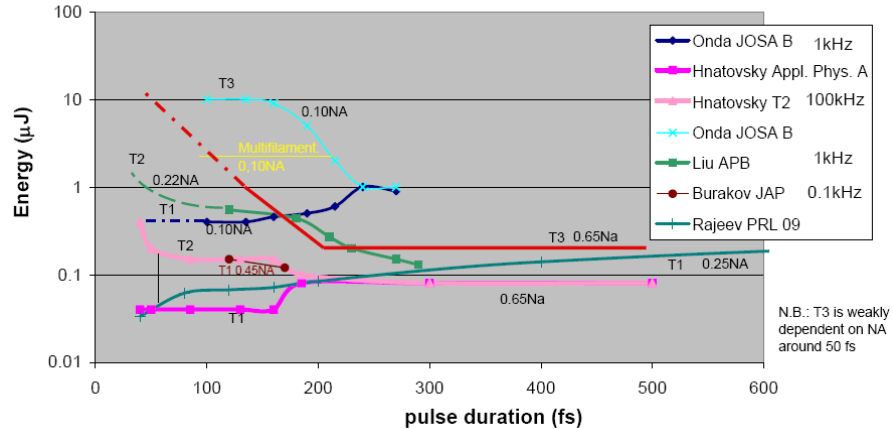


Fig. 7. collection of literature results on pulse duration whatever the repetition rate. Refs are the following: Onda JOSA B [66], Hnatovsky Appl. Phys. A [43], Liu APB [53], Burakov JAP [67] Rajeev PRL 09 [26].

Collapse of T2 with T1 means that silica decomposition is easily performed at large pulse duration. Even, T3 would collapse with the other thresholds for weak focusing. This is an important information for achieving a synthetic diagram according to NA for given pulse duration in section 4.5 and in section 5. Note also that T3 seems to become constant for small pulse duration and in addition independent on NA [66].

4.5 Dependence on Numerical Aperture NA

From the observation made above, we have to select results carefully according to pulse duration for determining the NA dependence of the thresholds. Collecting the results from the literature on the same graph, allows building Fig. 8 for T1 and Fig. 9 for T2. For a clear representation of all the results, we have used a log-log plot that seems to be suitable. The shift of the curves for a given NA is in agreement with the increase on pulse duration that we noticed in the previous section.

Again, here Schaffer et al. analysis is helpful for discussing NA dependence. T1 threshold appears to depend on NA strongly as shown by Ashcom et al. [68]. It is e.g. 0.025 μJ for NA = 1.4 but around 0.9 μJ for NA = 0.02. For NA > 0.1, The following expression can be used

again [55] give the following expression: $\frac{E_{th}}{\tau} = \frac{I_{th}\lambda^2}{\pi(NA)^2 + I_{th}2\pi n_0 n_2}$ in which I_{th} is the

intensity threshold ($3.2 \cdot 10^{13} \text{ W.cm}^{-2}$) for 60fs, 1kHz, 800 nm, $n_2 = 3.2 \cdot 10^{-16} \text{ cm}^2/\text{W}$. As we can see in [68], the T1 threshold departs largely from this formula for very weak focusing. This is due to plasma defocusing effect that becomes significant close and above the self-

focusing threshold ($P_{cr} = \frac{\lambda^2}{2\pi n_0 n_2}$ that means 0.11 $\mu\text{J}/\text{pulse}$ in the condition of Ref [68].). The

refractive index of the plasma is $n^2 = \varepsilon = 1 - \left(\frac{\omega_p}{\omega}\right)^2$, $\omega_p^2 = 4\pi \frac{\rho_{CB} e^2}{m_{CB}}$ where ρ_{CB} is the electron

density in the conduction band. So, as the density increases, the defocusing effect increases and slows down the critical self-focusing effect. It is thus necessary to increase the beam energy for reaching the optical breaking (T1 threshold). We can deduce that for strong focusing, the dependence is in $NA^{-1.9}$ whereas for lower NA, the dependence is rather $NA^{-0.8}$.

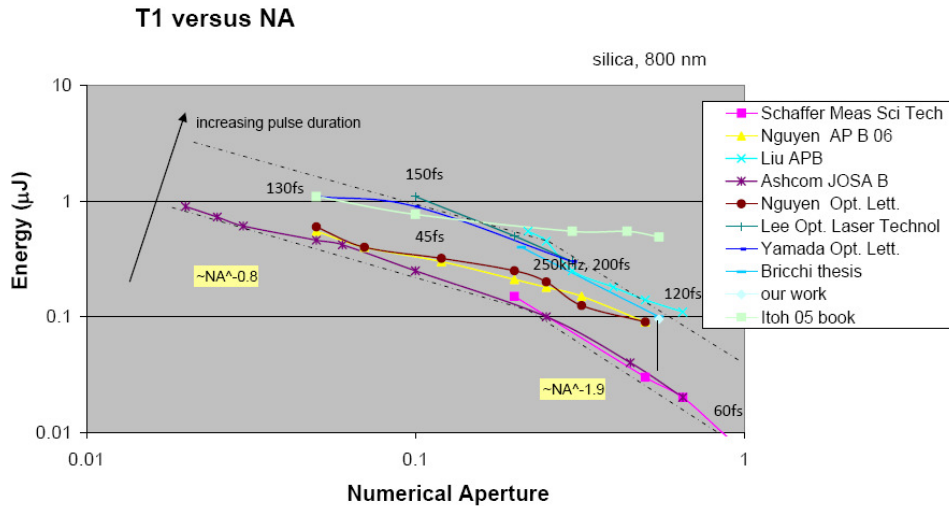


Fig. 8. Plot of T1 versus the numerical aperture of the lens used for focusing the laser beam. The dashed black lines are for showing the tendencies. The arrow indicates the direction of pulse duration increase. Refs are the following: Schaeffer Meas Sci Tech [55], Nguyen APB 06 [62], Liu APB [53], Nguyen Opt. Lett [69], Lee Opt. Laser Technol [70], Yamada Opt. Lett [71], Bricchi thesis [38,72], Our work [54], Itoh 05 book [10,73].

From the plot, it is clear that T_2 threshold depends on NA. It decreases when one increase the focal strength similarly to T_1 threshold and seems thus independent on the self-focusing threshold that is independent of NA. The dependency is however a little bit different than for T_1 (T_2 is different than T_1 for the pulse duration used in this graph): $T_2 \propto NA^{-1.2}$. The curve position is dependent on the pulse duration, decreasing when the pulse duration increases.

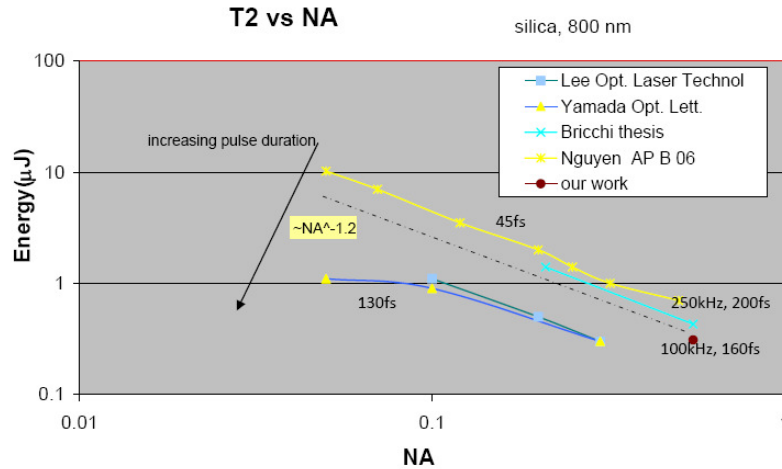


Fig. 9. Plot of T_2 versus the numerical aperture of the lens used for focusing the laser beam. The dashed black lines are for showing the tendency. The arrow indicates the direction of pulse duration increase. Refs are the following: Lee Opt. Laser Technol [70], Yamada Opt. Lett [71], Bricchi thesis [38,72], Our work [54], Nguyen APB 06 [62]

5. Sum-Up and Discussion

Combining all the observations made above in a consistent way, we can therefore tentatively elaborate Figs. 10–13 for pure silica. Despite the care we have taken for trying to conciliate all the results, they are probably not accurate but the purpose here is to show the tendencies. We have chosen to display the observation synthetically according to NA as log-log plots of pulse energy E versus NA for given laser wavelength, pulse duration, laser repetition rate because it shows most of the different domain of laser damages, their evolution according to the pulse duration and thus their possible use for practical applications. We have chosen four pulses durations corresponding to lasers mostly used and for which the areas of the regions change drastically: 45-60fs, 160fs, 200fs, and 250fs.

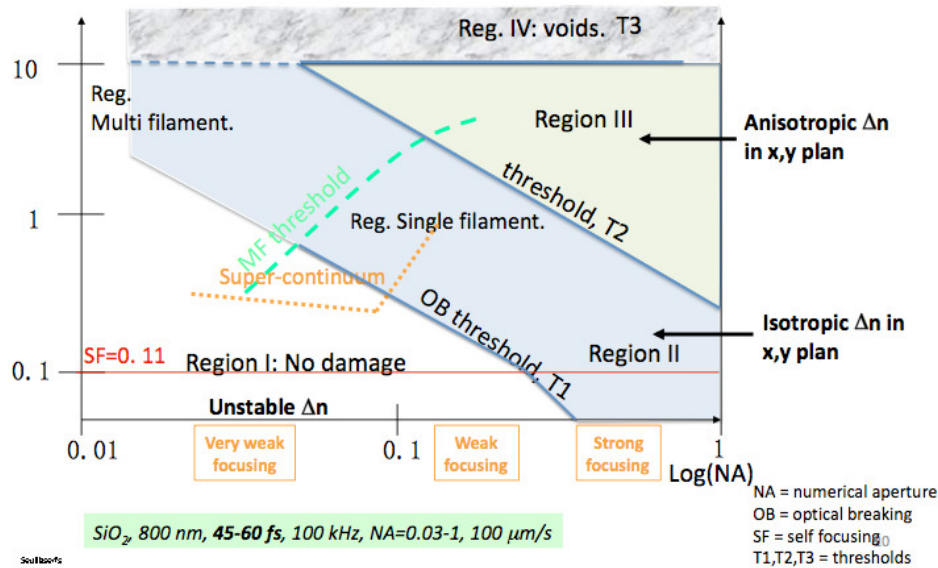


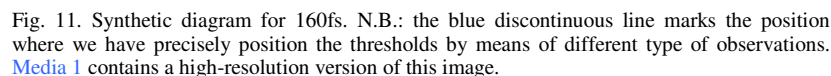
Fig. 10. Synthetic diagram for small pulse duration. Pulse energy versus Numerical aperture diagram in log-log scale defining regions with different kinds of laser interaction with silica. Laser parameters: 0.1-17 μJ , $\text{NA} = 0.01-1$, 45-60 fs, 100 kHz, 800 nm, polarization parallel to the scanning direction.

The threshold curves divide the plan into at least 4 regions. With small pulse duration, all regions are present. They will disappear one after the others when pulse duration is increased. For $\tau = 45-60\text{fs}$, in the region 1, below $T1$, no permanent damage is detected. Then, for $E > T1$, damages appear, the threshold decreases on NA and this is an interesting point as it is thus easy to make micro-machining with a moderate powerful laser. For $\text{NA} > 0.3$, for $T1 < E < 0.11 \mu\text{J}$, there is no filamentation and we can expect a compromise between short interaction volume with a maximum power. For $\text{NA} < 0.3$, $T1$ is above the self focusing (SF) threshold that is $P_{CR} \cdot \tau$ where $P_{CR} = \frac{\lambda^2}{2\pi n_0 n_2}$ and τ is the pulse duration, there is a single filamentation.

Above MF threshold (green curve in Fig. 10) multi-filamentation appears. There is also here a regime for which we can observe filamentation without observing damages. Another curve is shown on this diagram after [74], it is the threshold for super continuum generation, we can see that it is not associated with filamentation.

Below OB, the etching rate after laser irradiation is slow. For $\text{OB} < E < T2$, the etching rate is faster and clean (e.g. nothing remains in a laser processed trench). For $E > T2$, the etching rate is sensitive to the laser polarization state (2 orders of magnitude difference according to the polarisation) and part in the laser track is much faster etched than the others (what the authors call nanoplans) [75] (0.05-1 μJ , $\text{NA} = \text{unknown}$, 100 fs, 250 kHz, 800 nm). This is understandable as nanoplans are porous matter [8]. The optical scattering become stronger above [60] and (this is the most important), the refractive index changes becomes anisotropic.

For pulse duration around 160fs, threshold curves have moved. $T3$ moved down becoming dependent on NA for strong focusing. It results that it is easier to make voids. $T2$ moved down also, preserving the region III but this last decrease nevertheless. On the contrary, $T1$ curves moved up decreasing therefore the extension of region II for isotropic index change, considerably. In the same time, SF threshold increased from 0.11 to 0.35 μJ . Consequently, the region of index change without filamentation is enlarged.



A log-log plot showing the relationship between the logarithm of the electric field intensity, $\text{Log}(E) (\mu\text{J})$, on the y-axis, and the logarithm of the numerical aperture, $\text{Log}(NA)$, on the x-axis. The y-axis ranges from 0.1 to 10, and the x-axis ranges from 0.01 to 1. The plot is divided into several regions:

- Region I: No damage** (bottom left, white background)
- Region II** (top left, blue background)
- Reg. Single filament.** (middle left, light green background)
- Reg. IV: voids.** (top right, grey background)
- Region III** (bottom right, light green background)

Key features and thresholds:

- MF threshold for pulse duration < 230fs**: A dashed green line separating Region II from the single filament region.
- SF=0.44**: A horizontal red line indicating the self-focusing threshold.
- T1=T2** and **T3**: Diagonal lines representing thresholds for optical breaking and self-focusing, respectively.
- Anisotropic Δn in x,y plan**: Indicated by an arrow pointing to the boundary between Region III and Reg. IV.
- Unstable Δn** : Indicated by an arrow pointing to the boundary between Region III and Reg. IV.

Experimental parameters (bottom green bar): SiO_2 , 800 nm, 200 fs, 100 kHz, $NA=0.03-1$, 100 $\mu\text{m/s}$.

Legend:

- NA = numerical aperture
- OB = optical breaking
- SF = self focusing
- T1, T2, T3 = thresholds

Fig. 12. Synthetic diagram for 200fs. Note the narrow region II for isotropic index change.

Lastly for 250 fs pulse duration, there is no region of isotropic index in the diagram anymore. The down-shifting of T3 has considerably eaten the region of index change. These are the condition (250 fs and strong focusing, pulse energy<SF) for transversal microfluidic writing because filamentation is avoided. For longitudinal writing, weak focusing can be used. For larger pulse duration, this diagram will not change a lot as the threshold has become pulse independent. It is therefore possible to make nanoplanes until a few ps [76], for 0.5NA.

Kazansky group succeeded to write nanostructures at 1064 nm, 8ps, 0.5NA, 200kHz, 200-600 $\mu\text{m/s}$, whatever the configuration with energy larger than 0.8 μJ about and up to 2 μJ , value close to the maximum on our diagram.

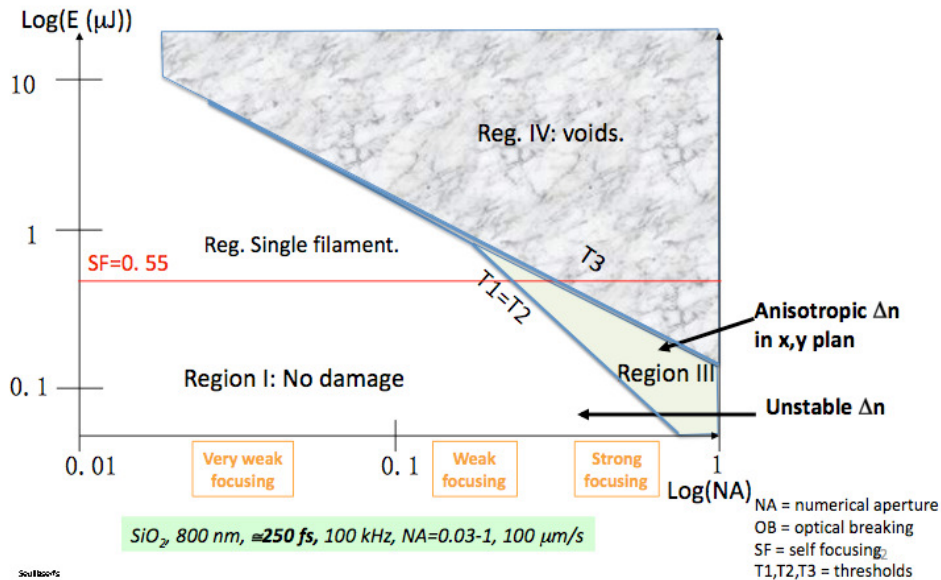


Fig. 13. Synthetic diagram for 250fs. Note that region II has disappeared.

We can notice from Fig. 2 and Fig. 4 if the repetition rate is decreased below 1kHz and the speed of writing increased above 100 $\mu\text{m/s}$, around 0.5NA, that a region II reappears as T1 and T2 are separated again.

6. Conclusions

Femtosecond laser effect in glasses is multifold depending on several parameters: energy (0.01-10 μJ), NA (0.01-1), τ (40-300fs), repetition rate (1kHz-1MHz), wavelength (IR 800-1080nm, UV). The permanent effects are numerous and some of them are specific of the femtosecond laser and SiO_2 : above T1 isotropic index appears, above T2 strong anisotropic index dominates, above T3 voids are formed. Analysis of the results from the literature allows determining changes of thresholds on laser parameters and thus help for finding optimized condition for achieving a specific one. On this way, we have tentatively established energy NA diagram according to pulse duration. Main interest at the moment is index change and micromachining but now other properties are aroused, like oxydo-reduction, cluster structuration and distribution with a sub-wavelength resolution. Some of the induced properties are quite new e.g. nanogratings, chirality, anisotropy, and strong dichroism. These qualities let us foresee a considerable development of the femtosecond laser writing technology.

Acknowledgments

This work has been performed in the frame of FLAG (Femtosecond Laser Application in Glasses) consortium project with the support of several organisations: the Agence Nationale pour la Recherche (ANR-09-BLAN-0172-01), the RTRA Triangle de la Physique (Réseau Thématique de Recherche Avancée, 2008-056T), FP7-PEOPLE-IRSES e-FLAG 247635 and the Essonne administrative Department (ASTRE2007) and the Ministry of the Foreign Affairs (PHC Alliance).